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Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.472233

Publication date:
1996

Document Version
Publisher's PDF, also known as Version of record

''Low-momentum electrons'' and the electronic structure of small molecules

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(Received 11 March 1996; accepted 20 May 1996)

The electronic Husimi distribution $\eta(\vec{r},\vec{p})$ is a ''fuzzy'' density in phase space. Sections through this function with a zero momentum variable ($\vec{p}=0$), are shown to be indicative of the spatial locations of chemical bonds and ''free electron pairs'' in molecules. The distribution $\eta(\vec{r};0)$ tends to focus on the inter-nuclear regions in position space. The Laplacian $\nabla_r^2\eta(\vec{r};0)$, of the function may be used to enhance its diffuse features. The argument is made that the momentum-space Hessian of the Husimi function at the momentum-origin ($\vec{p}=0$), includes information about the ''flexibility'' of the electrons and the anisotropy of the latter. The diagonalization of this tensor supplies a pictorial map of preferred directions of electrons in the low-momentum, i.e., ''valence'' region of momentum space. Examples studied in this paper include the H_2, N_2, CH_4, H_2O, C_2H_4 and C_6H_6 systems in their Hartree–Fock approximation. © *1996 American Institute of Physics.* [S0021-9606(96)00133-X]

I. INTRODUCTION: THE HUSIMI FUNCTION

In recent years, the quasiclassical phase-space description of many-electron systems has gained increasing attention as a means of combining real-space and momentum-space concepts for a more complete insight into atoms and small molecules on a one-particle level.[1–7] The motivation for such a description is that it promises to make both local and nonlocal information about an electronic system accessible in form of the classical notions of position and momenta. This information, contained in the (spin-traced) single-particle reduced density matrix (in the following, abbreviated ODM for ''one-particle density matrix'') $\rho(\vec{r};\vec{r}')$, may not be obtained from analysis of the familiar charge densities in position and momentum space alone, nor combined.

The way to arrive at such a description is to transform the ODM into a function of position and momentum, a reduced phase-space distribution. This transformation is not unique, and as a consequence, many distributions may be obtained and have been suggested.[8] They have in common that they may be used in combination with classical phase-space functions to obtain quantum-mechanical expectation values. The most well-understood of these distributions is also the oldest one: the Wigner distribution $W(\vec{r},\vec{p})$[9–13]

$$W(\vec{r},\vec{p})=\left(\frac{1}{\pi}\right)^3\int \rho(\vec{r}+\vec{s};\vec{r}-\vec{s})e^{-2i\vec{p}\cdot\vec{s}}\mathrm{d}\vec{s}. \tag{1}$$

Atomic units ($\hbar=1$) are used throughout, and consequently, factors of $\hbar$ are omitted. Among the possible phase-space representation, the Wigner function takes a special position, not only because of the symmetry and simplicity of its definition, but also because it fulfills conditions[10–13] which favor it before other alternatives.

Like most phase-space distributions that derive directly from Fourier-transformation of the ODM, the Wigner function has the position and momentum densities as its marginals, i.e., integration over one space yields the density in the other. However, orthogonality conditions[10] force this function to exhibit regions of negativity, which makes the interpretation as a probability distribution impossible. It may be argued that this problem overcompensates the close analogy to classical phase-space of the Wigner function, and that the lack of intuitive understanding has somewhat hindered its application as an interpretative tool in chemistry. It must be pointed out that alternative transforms of the ODM are also not positive everywhere, and that many of them are not even real-valued by definition.

The fact that it is impossible to assign a clear probability to points in phase-space, i.e., to define *positive definite* distributions that assign a probability of finding a particle at position $\vec{r}$ with momentum $\vec{p}$ is, of course, a consequence of the uncertainty principle of quantum mechanics. However, there exist distributions that include this principle in their definition, and consequently are positive everywhere. The most popular of those is the Husimi function $\eta(\vec{r},\vec{p})$,[4,14–16] which gives the probability of finding a particle in a coherent state (a so-called *state of minimal uncertainty*) centered at a given point in phase space. Its definition is, alternatively, a projection of the ODM onto a continuous basis of phase-space wave packets, or a Gaussian convolution of the Wigner distribution in both position and momentum space;

$$\eta(\vec{r},\vec{p})=\left(\frac{1}{2\pi}\right)^3\int \zeta^*(\vec{r},\vec{p};\vec{r}')\rho(\vec{r}';\vec{r}'')\zeta(\vec{r},\vec{p};\vec{r}'')\mathrm{d}\vec{r}'\,\mathrm{d}\vec{r}'' \tag{2}$$

$$=\left(\frac{1}{\pi}\right)^3\int \mathrm{e}^{-\sigma^2(\vec{r}'-\vec{r})^2}\mathrm{e}^{-(\vec{p}'-\vec{p})^2/\sigma^2}\times W(\vec{r}';\vec{p}')\mathrm{d}\vec{r}'\,\mathrm{d}\vec{p}', \tag{3}$$

where the wave-packet $\zeta(\vec{r},\vec{p};\vec{r}')$ represents the coherent state and is defined as

$$\zeta(\vec{r},\vec{p};\vec{r}\,')=\left(\frac{\sigma^2}{\pi}\right)^{3/4} e^{-\sigma^2(\vec{r}\,'-\vec{r})^2/2+i\vec{p}\cdot\vec{r}\,'}, \tag{4}$$

and σ^2 is a ''shape-factor'' that describes the degree of localization in position and momentum space. If $\sigma=\infty$, the Husimi function [properly renormalized with a factor of $(\sqrt{\pi}\sigma)^3$] reduces to the charge density, whereas $\sigma=0$ yields [after renormalization with $(\sqrt{\pi}/\sigma)^3$] the momentum density.[5]

It may easily be verified[4,15] that the uncertainties of $\zeta(\vec{r},\vec{p};\vec{r}\,')$ in position- and momentum-space fulfill the Heisenberg condition independently of σ^2, namely

$$\Delta r_i=\frac{1}{\sqrt{2}\sigma} \quad \text{and} \quad \Delta p_i=\frac{\sigma}{\sqrt{2}}, \tag{5}$$

and that therefore $\Delta r_i \Delta p_i = 1/2$, where i denotes any Cartesian component and r_i and p_i are conjugate coordinates. Setting $\sigma^2=1$ (as will be done throughout this paper) corresponds to a description, where position and momentum space are treated on an equal footing in atomic units.

Several favorable properties of the Wigner function have been given up in the Husimi distribution to achieve interpretability as a density; among them the charge and momentum densities as marginals, and the simple relationship to classical phase-space. The marginals of the Husimi function are Gaussian convolutions of the densities,[4,15] and expectation values may be derived from the Husimi function by finding the appropriate representation of the corresponding operators. This is equivalent to solving a deconvolution problem.[17] The gain is that $\eta(\vec{r},\vec{p})d\vec{r}d\vec{p}$ may be termed the probability of finding a particle *approximately* at position $\vec{r}$ with *approximately* a momentum of $\vec{p}$. The inherent ''fuzziness'' expressed in the term ''approximate'' is, however, clearly defined by Eqs. (2)–(4).

In recent years, the Husimi function was used repeatedly as a tool for the understanding of the effect of the chemical bond in molecular systems.[5–7] It is our belief that it may be used as a comparably simple concept for the unification of the two main descriptions in quantum chemistry. As an example for its applicability, we want to suggest the concept of ''low-momentum electrons'' in this paper.

II. ''LOW-MOMENTUM ELECTRONS''

Although the Husimi distribution may be interpreted more intuitively than the Wigner function, it still is a six-dimensional function, and as such does not easily lend itself for display. A possibility for the study of the ''shape'' of this function is the systematic investigation of its *critical points.* For this, the *gradient* of the Husimi function may be defined in the following manner:

$$\vec{\nabla}\,\eta(\vec{r},\vec{p})=\left\{\frac{\partial\eta}{\partial\mu}\right\}, \tag{6}$$

where μ denotes any component of $\vec{r}$ or $\vec{p}$. This is a six-component vector, and a characterization of $\eta(\vec{r},\vec{p})$ may be achieved by searching for $(\vec{r},\vec{p})$-vector pairs, for which this gradient vanishes ($|\vec{\nabla}\,\eta(\vec{r},\vec{p})|=0$). A complete list of such pairs, together with their classification in terms of eigenvalues and -vectors of its Hessian tensor (i.e., the 6×6-matrix of its second derivatives) at those points includes the basic information about the topology of the distribution. Research along those lines is currently being carried out.[18]

One of the findings from this type of study is that, for many systems, *all* extremal points in $\eta(\vec{r},\vec{p})$ are situated at the origin in momentum space, i.e., at $\vec{p}=0$. This is not surprising, remembering the fact that the momentum densities of small molecules exhibit only few critical points other than the origin (which has to be critical because of the inversion symmetry of momentum distributions[19,20]), and that these features are of a rather diffuse nature.[21–23] The convolution with a Gaussian of the order of 1 a.u. width [which is the momentum-space marginal of $\eta(\vec{r},\vec{p})$] is likely to exhibit only one central maximum at the origin with all other features ''washed out.'' However, this finding lends a particular importance to the momentum origin, an idea that was brought forward previously by other authors.[24]

The value of $\eta(\vec{r},0)$ focuses on those electrons that are approximately at rest. Sections through this ''low-momentum electron density'' (LMD) are therefore singling out those contributions to the electron distribution that are dominated by slow valence electrons. The typical distance of those valence electrons from the nuclei in a molecule is of the order of an Ångström, i.e., characteristic for bond lengths. These ''bond-regions'' are profoundly influenced by formation or breaking of bonds, in other words, by the underlying chemistry. It may be argued that the main energetic impact of bond formation arises from a net decrease of the potential energy, which is achieved by a contraction of the charge density in the vicinity of the nuclei (for a detailed discussion of the balance of effects, see Refs. 25 and 26). However, this *absolute* change takes place in regions were the charge density is very high and quite isotropic. The effect is therefore not particularly characteristic of the system and the changes it undergoes. On the other hand, it is usually accompanied by a great *relative* and strongly *anisotropic* change in the valence region, which also influences the kinetic part of the energy balance, and is very characteristic for the system specifics. It is therefore certainly chemically relevant to study functions that depend mainly on slow electrons. In the following, we will focus on $\eta(\vec{r},0)$ to substantiate these conjectures.

III. SOME EXAMPLES

We have computed the LMD and related quantities for a series of molecules from wave functions of self-consistent field (SCF) quality (dynamic electron correlation is therefore neglected). In comparisons with results from the singles/doubles configuration-interaction (SDCI) approximation, we did not find qualitative changes. The basis sets employed were of a ''triple-zeta with valence polarization'' (TZP) quality, and are standards included in the program HONDO-8,[27] with which all *ab initio* calculations were performed. The bond lengths and angles are experimental data from the literature (citations for the systems referred to: H_2

and N_2,[28] H_2O and CH_4,[29] C_2H_4,[30] C_6H_6[31]). No great influence of small changes in the molecular geometry is expected.

The LMD $\eta(\vec{r},0)$ for the hydrogen molecule (bond length of 1.40 a_0) does not exhibit any maxima at the site of the nuclei, but rather a single one at the bond midpoint. It is otherwise very featureless. Although the *independent atom model* (IAM), i.e., a simple superposition of atomic contributions at the same inter-nuclear distance, exhibits this concentration as well,[32] the effect is greatly enhanced in the molecule, and as a result, the difference density (molecule - IAM) is positive between the nuclear centers, and negative behind them. The total number of ''electrons at rest'' increases on bond formation, and very distinctly so on the bond (see Ref. 5, Fig. 5). This effect is equivalent to the one observed when comparing charge densities. The H_2 example was given previously by Anchell and Harriman,[5] and the effect expressed was called ''forward redistribution'': an increase between the nuclei and a depletion behind them.

One might expect similar effects in other molecules, but great caution is advised there. As was pointed out previously,[5] if a large contribution to the bond is owing to ''*p*-type'' atomic functions on the bound centers, the complete opposite may be observed for small values of $\vec{p}$, and thus for the LMD. A good example is N_2, where a complete ''reverse redistribution'' occurs (see Ref. 5, Section VI.2., Fig. 13 for a detailed analysis). It should also be kept in mind that each ''local momentum distribution'' at any given point $\vec{r}$ is normalized to the value of a convolution of the charge density at that point. As a result, the number-density of low-momentum electrons is influenced by both the relative number of electron approximately at rest, and the absolute number of electrons to be found approximately at that point. To separate one from the other, LMD would have to be divided by $\int \eta(\vec{r},\vec{p})\mathrm{d}\vec{p}$, yielding the ''percentage of electrons at rest.''

Our main interest, however, is the topology of the *total* LMD $\eta(\vec{r},0)$. It appears that maxima in this function occur *between*, rather than *at or near* connected nuclei. This is the case even for polyatomic molecules, and may be used to ''locate'' bonds. A rather striking example for this effect is the methane molecule. Figure 1(a) shows the distribution in a plane that passes through the carbon and two of the hydrogen nuclei. The maxima occur on the bond axis 1.34 a_0 away from C, whereas the bond length is 2.07 a_0. Note that the apparent maximum behind the carbon atom is really a saddle point [of the $(3,-1)$ type, to follow the notation of Bader[33]], connecting two bond-maxima out of plane. At the site of the nucleus itself, the function has a local minimum.

The situation is not always as clear as this. If the central atom is very electronegative, the bond maxima are less pronounced and may degenerate to shoulders. An example for this is found in the water molecule [Fig. 1(b)], where only a deformation of the LMD in the molecular plane indicates the presence of the O–H bonds. The maximum of the distribution is located slightly behind the oxygen nucleus (0.10 a_0), and is rather flat.

The natural means of enhancing features of such diffuse

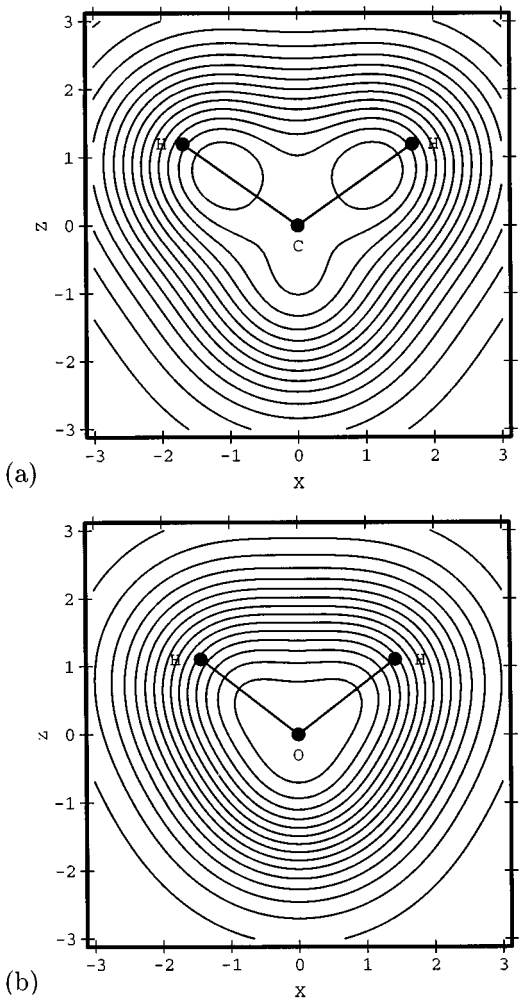

FIG. 1. Total LMD $\eta(\vec{r},0)$ for the CH_4 molecule at experimental bond length (2.065 a_0) (a) and for the H_2O molecule at experimental bond length (1.809 a_0) and angle (104.5°) (b). The central atom is at the origin of the coordinate system. The *z*-axes coincide with the molecular C_2 axes, and the depicted planes contain two hydrogen nuclei and the central atom. Contour lines are from 5×10^{-4} to 7.5×10^{-3} in steps of 5×10^{-4}.

distributions is the computation of their Laplacian; for the LMD we have

$$\nabla_r^2 \eta(\vec{r},0)=\left[\frac{\partial^2 \eta(\vec{r},\vec{p})}{\partial x^2}+\frac{\partial^2 \eta(\vec{r},\vec{p})}{\partial y^2}+\frac{\partial^2 \eta(\vec{r},\vec{p})}{\partial z^2}\right]_{\vec{p}=0}. \tag{7}$$

Local concentrations of ''low-momentum electrons'' will be visible in this distribution as negative areas. It must be pointed out that the stronger features of the Laplacian (as compared with the function itself) have a clear meaning; the value of the Laplacian is proportional to the difference between the local value of the function, and the average value in an infinitesimal surrounding.[34] In that sense, the Laplacian is a useful function to locate preferred areas in the distribution. It has been used in this capacity with great gain in the analysis of charge densities (see Bader's monograph[33] for many applications).

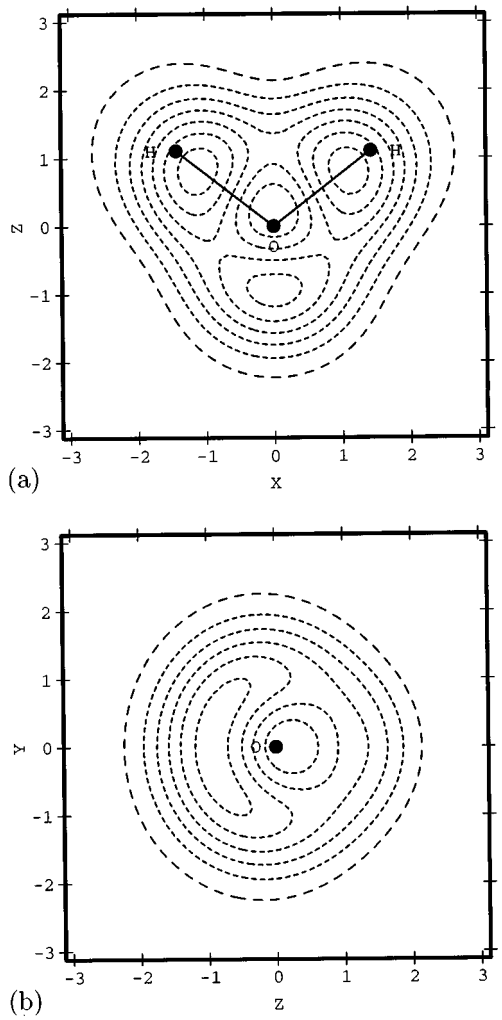

FIG. 2. Laplacian of the LMD $\nabla_r^2 \eta(\vec{r},0)$ for the H_2O molecule in the molecular plane (a) and perpendicular to it (b). The hydrogen atoms in (b) lie on the right-hand side. Contour lines are from -1×10^{-2} to 0 in steps of 2×10^{-3}.

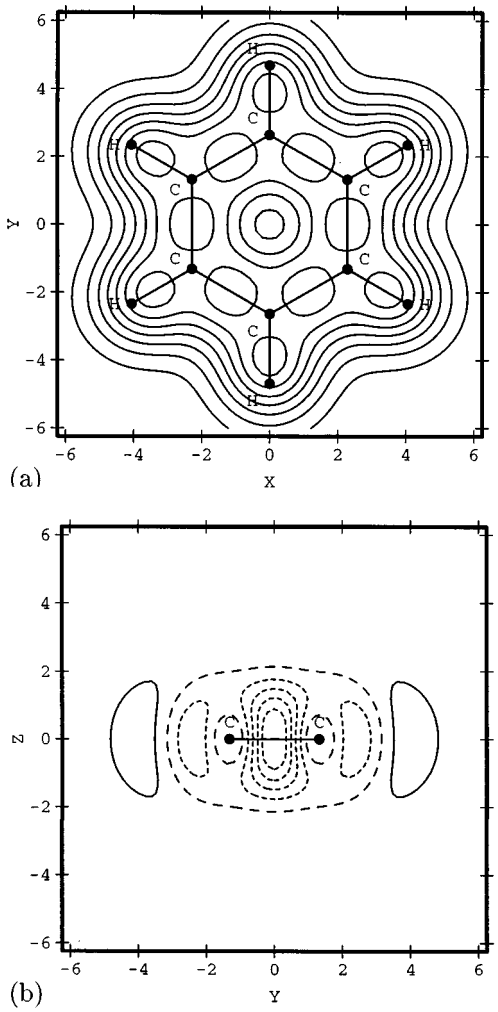

FIG. 3. (a) Total LMD $\eta(\vec{r},0)$ for the C_6H_6 molecule at experimental bondlengths (C–C: 2.640 a_0; C–H: 2.048 a_0) in the molecular plane. Contour lines are from 1×10^{-3} to 7×10^{-3} in steps of 1×10^{-3}. (b) Laplacian of LMD $\nabla_r^2 \eta(\vec{r},0)$ for the same molecule. The depicted plane is perpendicular to the molecular one, and passes through a C–C bond. Contour lines are from -8×10^{-3} to 2×10^{-3} in steps of 2×10^{-3}.

For water (Fig. 2), the Laplacian succeeds in making the bonds visible as minima. There is an additional minimum located behind the oxygen nucleus, which may be associated with the ''free electron pairs'' on oxygen in water. That this is so may be seen in the plane perpendicular to the molecular one, passing through the c_2 axis [Fig. 2(b)]. The negative region extends half-moon shaped behind the nucleus, i.e., in a region where conventional ''valence-shell electron-pair repulsion'' (VSEPR) arguments[35] would place the free electron pairs. It is indeed remarkable how similar the regions that we associate with bond and free electron pairs are to the ones obtained with the aid of the so-called ''electron localization function'' (ELF) suggested by Becke and Edgecombe.[36] This lends further credibility to the conjecture that chemically relevant information is expressed in LMD and its Laplacian. The negativity regions in Fig. 2 are even more strongly pronounced[37] than the corresponding ones in the Laplacian of conventional charge density (see, e.g., Ref. 33, p. 263, Fig. 7.5). The feature in the center is a local maximum, indicating the flatness of the maximum in the LMD itself [Fig. 1(b)]. This is not very surprising if one keeps in mind that in other comparable molecules (e.g., CH_4) one finds a local minimum of LMD in the vicinity of the central atom.

The last example in this section is the benzene molecule (Fig. 3). Distinct maxima in $\eta(\vec{r},0)$ (a) mark the C–C bonds, albeit slightly outwards from the line connecting two adjacent carbon nuclei [Fig. 3(a)]. The C–H bonds are also clearly expressed as maxima, 1.32 a_0 away from the carbon atoms (the C–H bond length is 2.05 a_0). The center of the molecule is of course a (3,+1) ring-critical point, i.e., a maximum only with respect to displacement perpendicular to the molecular plane. So are points in the close vicinity (0.08 a_0 ring-outwards) of the carbon atoms. All critical points lie in the plane. The Laplacian of the LMD exhibits strong minima on the C–H bonds (not shown), but the hydrogen atoms are ''invisible'' in both functions, i.e., they cannot be

associated directly with any separate extremal points.

The Laplacian may be used to more closely analyze the shape of the maxima in the LMD that are associated with each of the bonds. For this purpose a section through $\nabla_r^2\eta(\vec{r},0)$ perpendicular to the molecular plane is displayed in Fig. 3(b). It passes through a C–C bond axis (i.e., off-center). In contrast to the ''round'' and very diffuse C–H bond features, the negative region in $\nabla_r^2\eta(\vec{r},0)$ associated with this C–C bond is oblong in shape, a feature not visible in the LMD itself. This may be assigned to the partial π-character of that bond in the aromatic system. It is also observed in the shape of the Laplacian of the total charge density of this molecule. The Laplacian features several zero-value surfaces, which may be used to define a general shape of the molecule, since they separate (negative) regions where slow electrons accumulate, from regions that are depleted of them. For the benzene molecule, the latter is of course mainly the center of the ring and the vicinity of the carbon nuclei. Note that the positive regions are outwardly closed, since the Laplacian of any reasonable density has to approach zero asymptotically from above.

IV. ANALYSIS OF THE SHAPE IN MOMENTUM SPACE

The LMD selects a single point in momentum space, the origin, as representative. It has been pointed out by Kulkarni *et al.*[24] that this point is of particular importance for the topological analysis of molecular momentum distributions, particularly in the course of chemical reactions. However, the included information is necessarily restricted, a fact that may be seen as an advantage if only the ''slow'' valence regions are of interest. It is of course also possible to choose other momenta to gain more insight (see e.g., Ref. 5), but they would have to be chosen in each case separately.

Anchell and Harriman[6] recently gave a convincing example of how the total local momentum distribution, as defined by means of the Husimi function, may be used to assess the kinematic situation of electrons in specific regions of position space. They did this by analyzing the anisotropy of the Husimi kinetic-energy tensor. Since our study employs only one point in momentum space, the tensor describing the directional properties of our ''resting electrons'' has to be of a differential, rather than an integral nature. The obvious choice is the momentum Hessian $\mathbf{H}_p$ at $\vec{p}=0$;

$$H_{p;ij}=\left.\frac{\partial^2\eta(\vec{r},\vec{p})}{\partial p_i\partial p_j}\right|_{\vec{p}=0}. \tag{8}$$

Associated with this tensor is its trace, the Laplacian of the Husimi function in momentum space $[\nabla_p^2\eta(\vec{r},0)=H_{p;xx}+H_{p;yy}+H_{p;zz}]$. Its equivalent for the total momentum density $\pi(\vec{p})$ was the subject of some recent studies.[22–24,38–40]

The momentum-Laplacian $\nabla_p^2\eta(\vec{r},0)$ gives a measure for how strongly peaked a local momentum distribution is around the momentum origin. It has been argued that a local concentration of momentum signifies ''flexibility'' of the associated electrons,[39] an interpretation that was used for a conjecture concerning the conductivity in chemical systems.

One argument for this may be given in terms of a ''free particle at rest.'' In the absence of an external field, it is completely unrestrained, and its wave function is spread over all position space. On the other hand, the momentum-space analog is a δ-function at $\vec{p}=0$, with an infinite (negative) Laplacian. If the particle is subjected to an external attractive potential, its ''mobility'' decreases, it is more restricted and simultaneously, its momentum distribution broadens due to the uncertainty principle.[41]

As mentioned in Sec. III, the absolute value of the Laplacian is proportional to the difference between the local value of the density at a point and the average in its infinitesimal neighborhood.[34] For the momentum density of a bound system, the Laplacian therefore *decreases* with increasing strength of the binding. For example, if the external potential is harmonic (i.e., $V(\vec{r})=k|\vec{r}|^2$), the Laplacian scales with $k^{-5/4}$, whereas for a Coulomb field $[V(\vec{r})=-Z/|\vec{r}|]$, it goes with Z^{-5}. In any case, the stronger the particle is restrained, the smaller will be the magnitude of the Laplacian of the momentum density. This is true even if the value of the momentum density itself should be accidently zero (such as in *p*-states at the origin).

Another, equivalent, way of linking the Laplacian at $\vec{p}=0$ of a momentum distribution $\pi(\vec{p})$ to the ''mobility'' of the particles, is the realization that

$$\nabla^2\pi(0)=-(2\pi)^{-3}\int B(\vec{s})s^2\mathrm{d}\vec{s},$$

i.e., that it may be written as the *second moment* of the corresponding *autocorrelation function* $B(\vec{s})$. The latter is essentially a self-overlap of the one-electron wave function in position space, and therefore gives a measure for the ''range'' of the particle.[42–44] The weighting with s^2 particularly emphasizes large arguments, i.e., long-range effects. This is another formulation of the well-know reciprocity between position and momentum representation: strongly peaked (i.e., localized) distributions in one space correspond to diffuse behavior, i.e., large range and slow asymptotic decay in the other. However, a diffuse function in position space would certainly be considered ''softer'' or ''more flexible'' than a localized one.

Kulkarni *et al.*[22–24] relate $\pi(\vec{p})$ and its Laplacian at $\vec{p}=0$ to bond polarities and consequently to the ''ionic contributions'' to the wave function. They argue that a shift towards higher momenta and a drop in the value at the origin are a consequence of a ''biased'' charge distribution. Their examples[22] for covalently bonded symmetrical molecules generally show the most negative eigenvalue of the momentum Hessian at the origin associated with the main bond direction. Exceptions occur only for rather polar systems, and usually coincide with minima or saddle points at the origin.

These are considerations that argue *globally* on the basis of total momentum distributions. Our concern here is to apply them *locally*, i.e., point wise in position space. This may be done employing the Husimi function $\eta(\vec{r},\vec{p})$. Since the momentum Hessian $\mathbf{H}_p$ [Eq. (8)] is a tensor property, one may identify the direction of its main principal axis (i.e., the

direction of the eigenvector with the *most negative* eigenvalue) as the favorable one, or the direction of greatest mobility. However, since Husimi distributions are known to be very isotropic in momentum space,[4–7] any study of anisotropies depends on rather fine details. It is therefore favorable to subtract the isotropic value as a reference. In the following, we use a few small molecules to demonstrate how these concepts may help in interpreting LMD's further.

V. MOBILITY OF "LOW-MOMENTUM ELECTRONS": MORE EXAMPLES

There are, of course, various ways to display the information derived from the momentum-Hessian of $\eta(\vec{r},\vec{p})$. The method chosen here is to project the "main axis" (in this case the axis associated with the most *negative* eigenvalue of $\mathbf{H}_p$) pointwise onto a chosen plane of the system, and to choose its length proportionally to the anisotropy at that point. The advantage of this approach is that information about the "out-of-plane" components of the main axis are taken into account as well, since only if the latter is normal to the chosen plane, will its image reduce to zero. The disadvantage lies in the fact that *only* the main axis is considered. This may lead to discontinuities of the display around symmetry axes of the molecule; here, the eigenvalues are degenerate, and on either side of the symmetry element, different vectors (with different components in the displayed plane) are the main axis. We chose this method, since it seems to yield rather complete information, albeit at some expense of clarity. The length of the vectors are chosen proportional to the *absolute* anisotropy

$$\Delta\lambda = |\lambda_1 - \lambda_{\mathrm{av}}| = \left|\lambda_1 - \left(\sum_i \lambda_i\right) \Big/ 3\right| = \tfrac{1}{3}|2\lambda_1 - \lambda_2 - \lambda_3|, \tag{9}$$

where the indices i of the eigenvalues λ are taken to be in *ascending* order.

Only for a few very simple diatomic systems (see Fig. 4) is the "shape" of $\eta(\vec{r},\vec{p})$ around the origin of momentum space directly compatible with the *bond-directional principle* (BDP)[40,45–47] or its local version derived from the Husimi function.[6] The BDP expects momentum distributions to be elongated in directions *perpendicular* to the one of the chemical bond. Fig. 4(a) shows a map of "main mobility vectors" (MMV's), i.e., projections of the main axes of the $\mathbf{H}_p$ tensor for the hydrogen molecule. Far away from the nuclei, the vectors are always radial, both for atoms and molecules. They will also be quite small, since the anisotropy decreases, of course, with distance from the nuclear frame work. In the vicinity of the bond axis, however, the main direction is parallel to the bond, indicating that the "low-momentum electrons" in those regions are most "mobile" in *bond direction.* But only if the general shape of the local momentum distribution is assumed to be similar for all momenta, will this correspond to distributions that follow the BDP. This is the case for H_2 as the prototype of a simple covalent bond. The contour lines in the figures show the

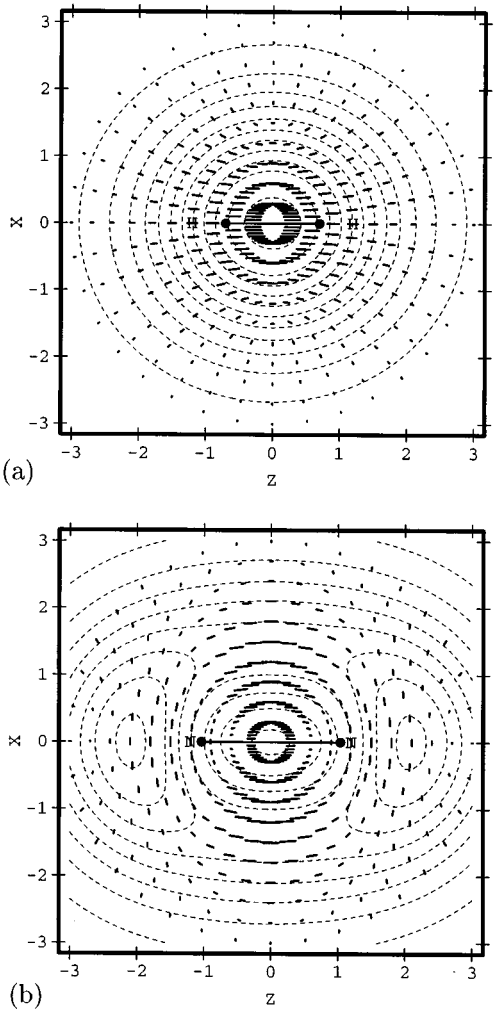

FIG. 4. (a) Momentum-Laplacian of the Husimi function at $\vec{p}=0$ (contour lines) and the associated MMV's in H_2 (experimental bond length 1.401 a_0). (b) Same for N_2 (experimental bond length 2.074 a_0). Contour lines are from -2.4×10^{-2} to -2×10^{-3} in steps of 2×10^{-3}. The scale of the vectors was chosen arbitrarily.

absolute size of the momentum-Laplacian $\nabla_p^2\eta(\vec{r},0)$. As expected, the most negative region is on-axis between the nuclei.

For multiply bonded diatomics, π-contributions will alter the picture somewhat by introducing perpendicular components in the vicinity of and behind the nuclei. The example of the N_2 molecule demonstrates this quite clearly [Fig. 4(b)]. Only far away from the molecule is the main axis oriented radially again. This finding, that the internuclear region exhibits local momentum distributions that are elongated perpendicularly to the bond, was demonstrated earlier[6] on the examples of CO and N_2. But again, the shape around the momentum-space origin may often not been taken as an indication of the anisotropy of the whole system. Note that in the nitrogen molecule [Fig. 4(b)], the bond midpoint is a local maximum in $\nabla_p^2\eta(\vec{r},0)$, indicating [in contrast to H_2; Fig. 4(a)] a lower flexibility between the nuclei as compared to the regions behind them.

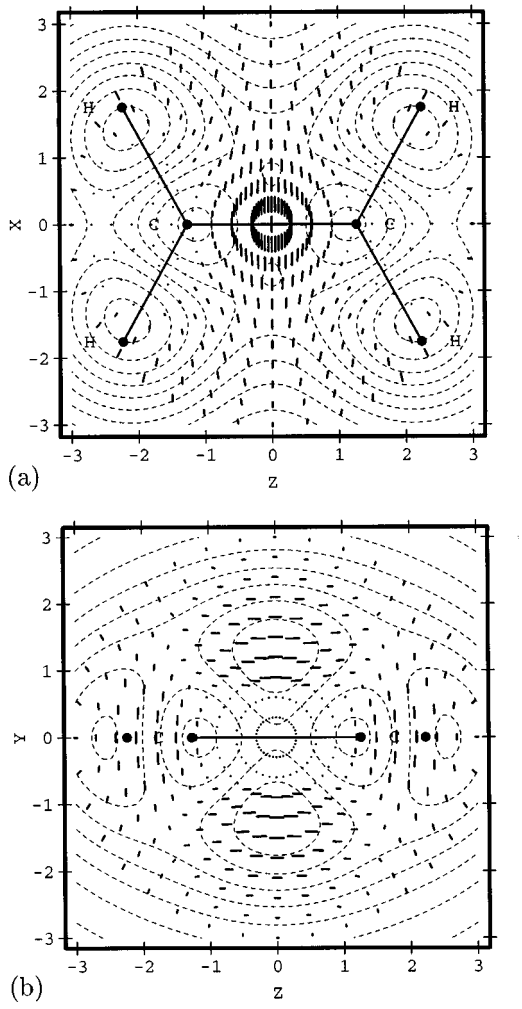

FIG. 5. Momentum-Laplacian of the Husimi function at $\vec{p}=0$ (contour lines) and the associated MMV's in C_2H_4. Bond lengths (experimental) C–C: 2.530 a_0 and C–H: 2.052 a_0; angle H–C–H: 117.6°. Contour lines are from -2×10^{-2} to -4×10^{-3} in steps of 2×10^{-3}. The scale of the vectors was chosen arbitrarily. Molecular plane (a), and plane perpendicular to it (b). The projection of the H-nuclei onto the plane are marked as unlabelled dots.

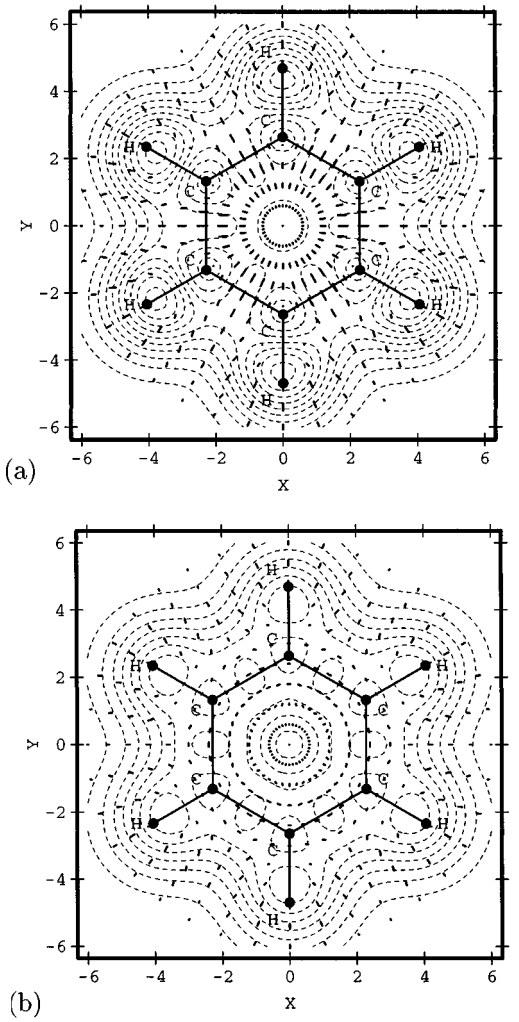

FIG. 6. Momentum-Laplacian of the Husimi function at $\vec{p}=0$ (contour lines) and the associated MMV's in C_6H_6. Bond lengths see Fig. 3. Contour lines are from -2×10^{-2} to -2×10^{-3} in steps of 2×10^{-3}. The scale of the vectors was chosen arbitrarily. Molecular plane (a) and plane parallel to the molecular one, but shifted by 1 a_0 (b). The nuclear frame was plotted for clarity, but lies below the depicted section.

Incompatibilities with kinetic-energy considerations (e.g., Ref. 6) occur frequently for more complicated molecular structures. The latter focus on high momenta (p^2-weighting of the momentum density in the kinetic-energy tensor), whereas we single out the *momentum origin.* For example, many hydrocarbons (e.g., Figs. 5 and 6) feature a preference of the MMV's of the ''low-momentum electrons'' in directions *perpendicular* to the C–H bonds. This tendency holds directly on the bond-axes, and even more so some distance away from it. Only rather close to (but still in front of) the hydrogen nuclei, in the region where the Laplacian $\nabla_p^2\eta(\vec{r},0)$ is minimal, does the parallel component win. This behavior must be specific for ''resting'' or slow electrons, since the total local momentum density is deformed in a perpendicular direction,[6] following the BDP. If the local momentum distribution near the C–H bond-midpoint is examined in detail, one finds that indeed only for small momenta a deformation *in bond direction* occurs, whereas for larger momenta, the BDP is observed. Apart from the systems shown, we found this phenomenon for methane, and both the staggered and the eclipsed conformation of ethane.

For ethylene (Fig. 5), there is a region in the arc between each of the carbons and the attached hydrogen centers, in which the MMV's are perpendicular to the molecular plane. Between the carbon centers, an anisotropy perpendicular to the bond, but in-plane is observed [Fig. 5(a)]. The situation perpendicular to the molecular plane is worth considering. In Fig. 5(b), a section through the mirror plane perpendicular to the molecular one is displayed. The momentum-Laplacian $\nabla_p^2\eta(\vec{r},0)$ exhibits two rather shallow minima above and below the molecule, which may be associated with the π-system. Around the carbon nuclei, maxima in the Laplacian are visible, and behind them (between the hydrogens) it is again minimal. The MMV's in the π-region are indeed aligned parallel to the bond, a phenomenon that is in accord

with chemical intuition, which would consider π-electrons most ''mobile'' in that direction. The total picture is that of a ring, passing perpendicularly through the nuclei and closing above and below the plane. The similarity with the nitrogen molecule [Fig. 4(b)] is obvious, but in the latter case, the π-system is cylindrically arranged around the bond axis, and the components perpendicular to this axis are overcome by it, whereas for C_2H_4, only one direction shows this effect, and the ''low-momentum electrons'' near the bond show a ''main mobility'' in-plane away from the bond.

In the benzene ring (Fig. 6), the main axis of $\mathbf{H}_p$ in the vicinity of the center, is perpendicular to the plane. This is no strong effect, i.e., the local momentum density there is almost isotropic around the momentum-origin. As one moves to the outside (but still in-plane), the radial component wins over, and the effect becomes stronger. It extends to infinity in all directions. However, in the region around the carbon nuclei, and partly extending into the C–H bonds, the preferred direction is perpendicular to the plane. This may be caused by the *p*-type symmetry of the valence one-electron functions on the carbon, and it is similar to the situation in the ethylene molecule (Fig. 5). No evidence of tangential components in the MMV's may be found in the molecular plane. Even in the C–C bond regions, the preferred direction is essentially radial. This is in contrast to intuitive expectations (which would have slow electrons most mobile in bond direction) and to the picture obtained in simple linear molecules. The topology of the momentum-Laplacian around each C–H unit is equivalent to the one in ethylene (Fig. 5).

There is only one area, in which the main-mobility direction is tangential, and that is below and above the plane in tori marking the π-system. This may be seen in Fig. 6(b), which shows the MMV-distribution and the momentum Laplacian in a plane parallel to the molecule, shifted by 1 a_0. Here, the familiar ''ring-current'' model of a benzene molecule, finds its expression. The effect, that the π-system of aromatic systems is rather ''conductive,'' is physically observable through increased magnetic susceptibilities and shifts in NMR. This has given rise to studies from the early days of quantum chemistry,[48,49] and up to recent times.[50,51] The restriction of tangential anisotropies to regions above and below the plane indicates that the σ-system has indeed no part in this phenomenon. Of course, caution is advised in comparing effects that depend on the presence of a magnetic field, by means of properties that depend only on the unperturbed ground-state wave function.

VI. CONCLUDING REMARKS

The picture of a molecule in terms of structure formulae, which forms the basis of our chemical understanding, is to a large degree a static one. That electrons in a chemical system are in constant movement, does not enter it directly, and this fact may be partly responsible for the preference that has been given to theoretical models based on the charge-density in position, rather than momentum space. Position and momentum densities are not equivalent, but complementary, i.e., it is not possible to convert one into the other without additional assumptions. Although in principle, either one of them determines all groundstate properties (see the famous Hohenberg–Kohn theorem[52] and its momentum-space equivalent by Henderson[53]), the functional form of this relationship is unknown, and the arising questions form the subject of a whole branch of quantum chemistry, density-functional theory (DFT).

A good deal of the problems with the interpretation of quantum chemical results arises from the fact that we cannot simultaneously assign position and momenta. The Heisenberg principle undermines an exact phase-space picture of molecular structure, and introduces ambiguities that may not be resolved easily. The Husimi function offers a controlled way of lowering our expectations on what we may find out about the state of electrons in a molecule by building the uncertainty relation that exits between their position and their momentum, into the representation. This function is still not unique, in that it is possible to focus on one space on the expense of the other, but one easily may arrive at a ''balanced'' description.

In this paper, we have attempted to single out the static aspects of electronic structure by focusing on electrons that are ''approximately at rest.'' It turns out that this admittedly narrow focus recovers indeed basic elements of chemical structure, namely the bonds. This is the result of a tendency of these electrons to accumulate between nuclei that are covalently bonded to each other. It shares this feature with descriptions on the basis of the one-particle density matrix,[54,55] from which it is derived. The description is certainly not complete: polar bonds are often not seen as maxima in the associated distribution $\eta(\vec{r},0)$, but lead at least to accumulative features which may be enhanced by means of the Laplacian $\nabla_r^2 \eta(\vec{r},0)$.

The usage of the latter is a standard tool of functional analysis. It is suitable to detect regions which are preferred by the distribution relative to neighboring ones. Its interpretation as a local excess or a local concentration makes it a rather powerful tool to visualize such entities as ''free electron pairs'' and ''bond regions,'' if it is applied to the LMD. The resulting features are in some cases reminiscent to earlier approaches[36] which are based on completely different concepts.

The analysis of the shape of a local momentum distribution in the close vicinity of the ''point of rest,'' i.e., the origin of momentum space, is enabled by the Hessian tensor $\mathbf{H}_p$ of the Husimi distribution at that point. A conjecture, made first by MacDougall,[39] that links the size of the momentum Laplacian $\nabla_p^2 \eta(\vec{r},0)$ to electron flexibility is used in the interpretation of the anisotropies of the local momentum density for very small momenta. Although in some simple cases, familiar concepts such as the bond-directional principle are reflected in the resulting ''main mobility vectors'' (MMV's), many features are specific to the very slow region of momentum space and do not coincide with the intuitive expectations. In some cases, however, interesting results are obtained with this approach. We find distinct regions in unsaturated hydrocarbons that may be associated with their π system; the preference for tangential mobility in ring-shaped

regions above and below the molecular plane of aromatic systems is another example.

We hope that the particular point of view that arises from the study of these sections through the Husimi function adds to a more ''holistic'' understanding of the one-particle structure of molecules. The parallels between features of phase-space descriptions such as the one employed here, and rather diffuse concepts of basic chemical knowledge, support the hope that many of those concepts can be linked to the quantum mechanical description of chemistry. Such links, if nothing else, contribute to a better understanding between ''molecular physicists'' and ''straight chemists.''

ACKNOWLEDGMENTS

The financial support that made this work possible comes from the Danish Natural Science Research Council. The *ab initio* calculations used here where preformed with the installment of the program HONDO in the theoretical chemistry group at Queen's University in Kingston, Ontario. I have more than that reason to thank Dr. Vedene H. Smith, Jr., who heads that group. I would also like to acknowledge the support and suggestions of Dr. Jens-Peder Dahl. The suggestion to examine Laplacians of the Husimi function was made by Dr. John E. Harriman, who, apart from being the first to conduct detailed studies on the electronic Husimi function of molecules, also helped in bringing this paper ''into shape.'' I am very grateful for that.

Parts of this paper were given as a poster presentation at the ''6th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics,'' Paris, August 1995.

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